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A simple theory for thermodynamics of liquids

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Abstract : A simple theory for the thermodynamic properties of liquids is developed, based on the physical interpretation of the reciprocal of activity. Expressions for the effective pair potentials are derived for different thermodynamic properties of the fluid. The theory is applied to estimate the effect of the triple dipole potential on the equation of state and excess free energy of the liquid. The effect of the triple dipole potential, which increases with the increase of the atomic mass, is found to be small.

Keywords : Effective pair potential, triple dipole potential.

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1. Introduction

The present paper is concerned to estimate the effect of three-body forces on the thermodynamic properties of dense fluids or liquid. In condensed state, the assumption of pairwise additivity of the intermolecular potential is approximate even for the simplest real fluids (the inert gases) [1]. So it is necessary to include at least the three-body interaction. In the usual approach, the effect of the three-body interaction is included by replacing the bare pair potential with an effective pair potential [2,3], which may be a function of temperature and density. It is found that different properties lead to different effective pair potentials [3].

Using the pairwise additivity of the total potential, Andrews developed simple method for evaluating the thermodynamic properties of dense fluids, based on a physical interpretation of the reciprocal of the activity, which is derived from the partition function. The basic physical concept associated with this approach is that, for a dense fluid or liquid, the repulsive forces (which are nearly hard sphere interactions) dominate the fluid structure, and the attractive forces play a minor role. In this paper, we extend this approach to include the three-body interaction potential. This approach provides a simple way of defining the effective pair potential and calculating the thermodynamic properties and gives a good physical interpretation of the model.

2. Theory of liquid in the presence of three-body forces

We consider a classical liquid, for which the total potential energy is written as

$$\Phi(1,2,.....N) = \sum_{i<j} u(i,j) + \sum_{i<j<k} u(i,j,k), \qquad (1)$$

where $u(i, j)$ and $u(i, j, k)$ are the pair and triple potential energy, respectively. Under this assumption, the canonical partition function can be written as

$$Q_N = (N!\lambda^{3N})^{-1} \int....\int \prod_{i<j} (1+f_{ij}) \prod_{i<j<k} (1+K(i,j,k)) \prod_{i=1}^{N} dr_i , \qquad (2)$$

where

$$f_{ij} = \exp\,[-\beta u(i,j)] - 1, \qquad (3a)$$

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$$K(i, j, k) = \exp[-\beta u(i, j, k)] - 1. \quad (3b)$$

Here, λ is the thermal wavelength and $\beta = (kT)^{-1}$ (k is the Boltzmann constant and T the absolute temperature).

The chemical potential μ of the classical fluid can be obtained from the partition function by the relation

$$\beta\mu(\beta,\rho) = -(\partial \ln Q_N/\partial N) = -[\ln Q_{N+1}/\ln Q_N]. \quad (4)$$

Substituting eq. (2) in eq. (4) and following the method of Singh and Sinha [6], we obtain

$$\beta\mu = \beta\mu_{id} + \beta\mu_{ex}, \quad (5)$$

where

$$\beta\mu_{id} = -\ln(V\lambda^{-3}/N) = \ln(\rho\lambda^3), \quad (6)$$

$$\beta\mu_{ex} = \ln a, \quad (7)$$

with

$$Va^{-1} = \int dr_{N+1} \prod_{i=1}^{N} (1 + f_{iN+1}) \prod_{i<j}^{N} (1 + k(i, j, N+1)). \quad (8)$$

Here, a is the activity of the fluid relative to the ideal gas at same T and ρ. Eq. (8) shows that the N particles are fixed in a most likely configuration and the $(N + 1)$st particle wanders throughout the entire system. The physical interpretation of eq. (8) has been used by Andrews [4,5] to give an expression of the equation of state of the classical fluid using the pair potential. It has been used by Singh and Sinha [6,7] to evaluate the thermodynamic properties for the semiclassical fluid. We extend this approach for the classical fluid in the presence of the three-body forces and write

$$a^{-1} = a_{HS}^{-1} \exp\left[\rho \int^{\tau} (dr_2 f_{12} + (1/2))\rho^2 \int^{\tau} (dr_2 dr_3 K(1,2,3) \times (1 + f_{12})(1 + f_{23})\right] \quad (9)$$

where a_{HS}^{-1} is a^{-1} for the hard sphere (HS) fluid and given by [4]

$$a_{HS}^{-1} = (1 - 0.74053) \exp[-5.1834z/(1 - 1.5340z + 0.5340z^2)], \quad (10)$$

where $z = \rho d^3/\sqrt{2}$, d is the hard sphere diameter and τ is the potential cut-off. Here $\rho = N/V$ is the number density.

From eqs. (7) and (9), the expression for the excess chemical potential is

$$\beta\mu_{ex} = \beta\mu_{ex}^{HS} - \rho \int^{\tau} (dr_2 f_{12} + (1/2)\rho^2 \int^{\tau} (dr_2 dr_3 K(1,2,3) \times (1 + f_{12})(1 + f_{23}), \quad (11)$$

where μ_{ex}^{HS} is the excess classical potential of the HS fluid

$$\beta\mu_{ex}^{HS} = -\ln a_{HS}^{-1} = (5.1834z/(1 - 1.5340z + 0.5340z^2)) - \ln(1 - 0.7405z). \quad (12)$$

Other thermodynamic properties can be obtained from eq. (9). Andrews [4,5] obtained expression for pressure in terms of $\ln a^{-1}$ as [see eq. (6) of Ref. 4]

$$\beta P/\rho = 1 - \ln a^{-1} + (1/\rho) \int_0^{\rho} \ln a^{-1} d\rho. \quad (13)$$

Substituting eq. (9) in eq. (12), we obtain an expression for the equation of state

$$\beta P/\rho = \beta P_{HS}/\rho - (1/2)\rho \int^{\tau} (dr_2 f_{12} + (1/3))\rho^2 \int^{\tau} (dr_2 dr_3 \times [1 + K(1,2,3)](1 + f_{12})(1 + f_{23}), \quad (14)$$

where P_{HS} is the pressure of the classsical HS fluid and given by [4]

$$\beta P_{HS}/\rho = 5.1834z/(1 - 1.5340z + 0.5340z^2) - (1.3504z) \ln(1 - 0.7405z) - (4.8534/z) \ln(1 - 1.5340z + 0.5340z^2) - (15.977/z) \ln((1 - 0.5340z)/(1 - z)). \quad (15)$$

Singh and Sinha [7] expressed the excess free energy in terms of $\ln a^{-1}$ as

$$\beta\Delta F/N = -(1/\rho) \int_0^{\rho} \ln a^{-1} d\rho. \quad (16)$$

Using eq. (9) in eq. (16), we obtain an expression for the excess free energy as

$$\beta\Delta F/N = \beta\Delta F_{HS}/N - (1/2)\ \rho \int^{\tau} (dr_2 f_{12} - (1/6))$$

$$\times \rho^2 \int_d^\tau (dr_2 dr_3 (1 + K(1,2,3)(1 + f_{12})(1 + f_{23}), \quad (17)$$

where ΔF_{HS} is the excess free energy of the HS fluid and given by [7]

$$\beta\Delta F/N = 1 - \ln(1 - 0.7405z) + (1.3504/z) \times \ln(1 - 8.7405z^2) + (4.8534/z) \times \ln(1 - 0.5340z)/(1 - z)). \quad (18)$$

Eqs. (11), (14) and (17) can be expressed in simpler forms in terms of the effective Mayer function. Thus

$$\beta\mu_{ex} = \beta\mu_{ex}^{HS} - \rho \int_d^\tau dr_2 f_{12}^{\mu}, \quad (19)$$

where

$$f_{12}^{\mu} = f_{12} + (1/2)\ \rho \int dr_3\ K(1,2,3)(1 + f_{13}) \times (1 + f_{23}), \quad (20)$$

$$\beta P/\rho = \beta P_{HS}/\rho - (1/2)\rho \int_d^\tau dr_2 f_{12}^{p}, \quad (21)$$

where

$$f_{12}^{p} = f_{12} + (2/3)\ \rho \int dr_3\ K(1,2,3) \times (1 + f_{13})\ (1 + f_{23}) \quad (22)$$

and

$$\beta\Delta F/N = \beta\Delta F_{HS}/N - (1/2)\rho \int_d^\tau dr_2 f_{12}^{e}, \quad (23)$$

where

$$f_{12}^{e} = f_{12} + (1/3)\ \rho \int dr_3 K(1,2,3)(1 + f_{13})(1 + f_{23}). \quad (24)$$

Thus we get different effective Mayer functions for different thermodynamic properties of the fluids. The effective pair potentials are obtained from the effective Mayer functions by the relation

$$u^{\mu}(1,2) \approx u(1,2) - (1/2)kT\ A(1,2), \quad (25)$$

$$u^{p}(1,2) \approx u(1,2) - (2/3)kT\ A(1,2), \quad (26)$$

$$u^{e}(1,2) \approx u(1,2) - (1/3)kT\ A(1,2), \quad (27)$$

where

$$A(1,2) = \rho \int dr_3 K(1,2,3)(1 + f_{13})\ (1 + f_{23}), \quad (28)$$

From this discussion, we find that the effective pair potential is not unique; different properties lead to different effective pair potentials, as discussed earlier [3]. This approach is expected to provide good results for dense fluids or liquids.

3. Effective pair potentials and hard sphere diameter

We represent the pair interaction by the Lennard-Jones (LJ) (12–6) potential

$$u_{LJ}(r) = 4\epsilon_0[(\sigma_0/r)^{12} - (\sigma_0/r)^6], \quad (29)$$

where ϵ_0 represents the depth of the potential well and σ_0 the diameter of the molecule and the three-body interaction is the dipole-dipole potential of Axilord and Teller [8], given by

$$u(1,2,3) = \left[\nu/(r_{12}^3 r_{13}^3 r_{23}^3)\right][1 + 3\cos\theta_1 3\cos\theta_2 3\cos\theta_3], \quad (30)$$

where r_{12}, r_{13}, r_{23} are sides and θ_i is the angle of the triangle at the corner i, and ν is the interaction coefficient, depending on the atomic species.

We divide the pair potential $u_{LJ}(r)$ into the reference part $u_r(r)$ and perturbation part $u_p(r)$ according to Weeks, Chandler and Anderson (WCA) scheme [9]. The properties of reference system can be obtained in terms of these expansion of a HS system of the hard sphere diameter d given by Verlet and Weis [10].

The equation of state of the HS fluid is calculated using eq. (15). To estimate the contribution of the three-body interaction, we write

$$Z(r_{12}) = -(2\pi/r_{12})\rho\beta \int_d^\tau \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} u(1,2,3) \times \exp[-\beta(u(r_{13}) + u(r_{23}))]\ r_{13} dr_{13} r_{23} dr_{23}. \quad (31)$$

Knowing z, we obtain the effective pair potential for different thermodynamic properties of the fluid. Then the contribution of the attractive tail is evaluated.

4. Results and discussion

We employ the theory to calculate the thermodynamic properties of the fluid in the presence of the triple-dipole interaction.

We first test the accuracy of the theory. We employ this theory to calculate the equation of state, $\beta P/\rho$ for the LJ(12–6) fluid and compare the results with the exact Monte Carlo (MC) data [8] in Table 1. The agreement is found to be good. Hence, this theory can be used to

Table 1. Comparison of the equation of state $\beta P/\rho$ of the LJ(12–6) fluid with the exact data.

ρ^*	T^*	Present theory	Exact
0.30	1.35	0.355	0.35
0.40	1.35	0.301	0.27
0.55	2.74	1.708	1.65
0.65	1.04	–0.145	–0.11
0.70	1.35	1.129	1.17

study the effect of the triple-dipole potential for some real fluids like Argon (Ar), Krypton (Kr) and Xenon (Xe).

The values of $\beta P/\rho$ for these fluids are reported in Table 2 for different reduced density $\rho^* = \rho\sigma_0^3$ at reduced temperature $T^* = kT/\epsilon_0 = 0.80$, 1.15 and 2.74,

Table 2. Values of $\beta P/\rho$ for the LJ(12–6) fluid in the presence of the triple-dipole potential.

T^*	ρ^*	$\beta P_{LJ}/\rho$	$\beta P/\rho$		
			Ar	Kr	Xe
			$\nu^* = 0.075$	$\nu^* = 0.090$	$\nu^* = 0.099$
0.80	0.30	−0.974	−0.921	−0.910	−0.903
	0.50	−1.505	−1.357	−1.328	−1.310
	0.70	−0.548	−0.261	−0.204	−0.170
	0.90	4.134	4.600	4.693	4.749
1.15	0.30	0.103	0.137	0.144	0.148
	0.50	0.203	0.298	0.317	0.328
	0.70	1.559	1.743	1.780	1.802
	0.90	5.839	6.138	6.198	6.234
2.74	0.30	1.147	1.159	1.161	1.162
	0.50	1.753	1.785	1.792	1.796
	0.70	3.169	3.231	3.244	3.251
	0.90	5.989	6.088	6.108	6.120

along with the LJ(12–6) values. We find that the effect of the triple-dipole potential which is positive increases with the increase of the atomic mass and density ρ^* and decrease of temperature T^*.

The values of $\beta\Delta F/N$ for Ar, Kr and Xe are demonstrated in Table 3 at $T^* = 0.80$, 1.15 and 2.74.

Table 3. Values of $\beta\Delta F/N$ for the LJ(12–6) fluid in the presence of the triple-dipole potential.

T^*	ρ^*	$b\Delta F_{LJ}/N$	$b\Delta F/N$		
			Ar	Kr	Xe
			$\nu^* = 0.075$	$\nu^* = 0.090$	$\nu^* = 0.099$
0.80	0.30	−2.196	−2.169	−2.164	−2.161
	0.50	−3.379	−3.305	−3.290	−3.282
	0.70	−4.166	−4.023	−3.994	−3.977
	0.90	−4.225	−3.992	−3.945	−3.917
1.15	0.30	−1.099	−1.082	−1.078	−1.076
	0.50	−1.577	−1.529	−1.520	−1.514
	0.70	−1.709	−1.617	−1.598	−1.587
	0.90	−1.236	−1.086	−1.056	−1.038
2.74	0.30	−0.008	−0.002	−0.000	+0.000
	0.50	0.176	0.192	0.195	0.197
	0.70	0.605	0.636	0.642	0.646
	0.90	1.236	1.286	1.296	1.302

The corresponding values of the LJ(12–6) fluid are also shown there. The effect of the triple interaction on the excess free energy is positive in this case also.

5. Conclusions

In previous study [3] same effective potential is used for different properties. In the present paper, we have obtained different effective potentials for different thermodynamic properties. Sinha *et al* [3] in 1985 have done exhaustive work on the three-body forces. After 1985, no work is available on the three-body forces.

We have developed the simple theory in the presence of the three-body potential, based on the physical interpretation of the reciprocal of the activity. The effective pair potentials are derived for the different thermodynamic properties.

The theory is applied to estimate the effects of the triple-dipole potential on the thermodynamic properties of dense simple fluids such as Ar, Kr and Xe. From the study, we find that the effect of the triple potential, which increases with the atomic mass and density, and decrease of temperature, is small. The assumption of pair-wise additivity of the interaction can be employed for dense fluids or liquids.

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